Enthalpies of Vaporization of Organic Compounds*

VIII. Alkoxyethanols

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Enthalpies of vaporization have been measured calorimetrically
at 25°C for a number of alkoxyethanols, $ROCH_2CH_2OH$, R = Me,
Et, Pr, i-Pr, Bu. Vaporization values have been correlated with
structural parameters and with normal boiling points.

The present report is part of a calorimetric study on the enthalpies of vaporization of organic compounds at 25°C. The aim is to study particularly important groups of compounds and to provide a basis for empirical methods used for the estimation of this kind of data.

In a recent paper enthalpies of vaporization for a number of disubstituted ethylene glycoles were reported.[2] Here, results are presented from measurements on a series of ethylene glycol monoethers, $ROCH_2CH_2OH$. These compounds, like the disubstituted glycols, are of great practical importance as they are extensively used as industrial solvents.

Several ΔH_v values have been reported in the literature for 2-methoxyethanol ("methyl cellosolve") and 2-ethoxyethanol ("cellosolve"). However, most of these are poorly documented and show a large spread and were judged to be unreliable. As pointed out by Bondi and Simkin[3] the purities have probably not been adequate in these earlier studies. During the present study it became apparent that these compounds are very hygroscopic. When dry, methoxyethanol and ethoxyethanol in particular adsorb moisture from the air at a very fast rate. It is doubtful if this has been realized in earlier studies and we therefore suspect that physico-chemical data in general may be unreliable for these compounds.

EXPERIMENTAL

Materials. 2-Methoxyethanol was kindly supplied by Mo and Domsjö AB. All other starting materials were commercial samples of puriss. grade (Fluka). The substances

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were dried over molecular sieves, 4A, and were fractionally distilled three times or more under reduced pressure. Distillation temperature was in all cases about 100°C and a 15 plate column was used. The last fraction collected was again dried over molecular sieves and was finally distilled in a simple outfit. The samples were transferred by a distillation procedure into dry glass ampoules. The samples were sealed off under dry nitrogen. In the case of methoxyethanol some samples were transferred and sealed under vacuum. No difference in the water content was found between the two methods.

The purification process was followed by gas chromatographic analysis using Varian Aerograph 600 D; 5' × 1/8" column of Carbowax on Chromosorb W. The purities of the samples used in the calorimetric determinations were judged to be better than 99.85 mole%. Water content was also determined by gas chromatography using a Porapak Q column. In all cases the water content in the sealed ampoules was less than 0.02 weight%.

Calorimetric measurements. The calorimeter and the general calorimetric procedure have been described in detail elsewhere.[4] Before and after the calorimetric measurements, samples were taken out from the calorimeter and analyzed for water content. The procedure was as follows. By use of a dried 1 ml syringe *ca.* 0.3 ml of sample was quickly transferred from the ampoule to the calorimeter. The filling tube of the calorimeter was closed and a precession movement given to the calorimeter so that the substance wetted the walls of the vaporization chamber. Subsequently 30 μl of the sample was withdrawn from the calorimeter by a chromatographic syringe. The tip of the needle was immediately closed by a silicone stopper and the sample was quickly analyzed for water. The calorimeter was weighed and the measurement carried out in the usual manner. Immediately after the weighing of the calorimeter following the calorimetric experiment a second sample was taken and analyzed.

If the vaporization measurement was carried out as described in Ref. 4 the second sample had a significantly higher water content than the starting material. This was particularly the case for methoxy- and ethoxyethanol. No significant increase in the water content was noted during the equilibration period prior to the experiment and it is therefore believed that the moisture was transported to the calorimeter by the carrier gas. This was earlier routinely allowed to pass Drierite tubes positioned close to the nitrogen cylinder. The gas was then transported through vinyl tubings to the pressure regulating system and from there to the calorimeter. Drierite was in this work replaced by a more powerful desiccant, Anhydron, and the drying tubes were placed immediately before the metal tubes extending from the calorimeter (*cf.* Ref. 2). Using these precautions the water uptake was very significantly reduced for all the investigated compounds. However, for the methoxyethanol and ethoxyethanol the water uptake was still too high to be neglected. The experimental results for these compounds were therefore treated by a separate procedure.

Calculation of results for MeOCH$_2$CH$_2$OH *and* EtOCH$_2$CH$_2$OH. Assume that the calorimeter in an experiment is charged with *a* g of substance containing *x* weight% of water and that *b* g containing *y* weight% of water remains in the calorimeter after the vaporization. The weight of pure compound evaporated is thus $a(1-0.01 x)-b(1-0.01 y)$ g, and the amount of water taken up by the liquid will be $0.01(by-ax)$ g. This water was originally present as a gas and became solvated by the compound during the experiment. The water solvation process can be looked upon as a condensation of the water followed by a solution into the substance. The heat balance for the vaporization experiment can thus be written as

$$q = [a(1-0.01x)-b(1-0.01y)] \, \Delta h_v - 0.01(by-ax) \, \Delta h_v'$$
$$- 0.01(by-ax) \, \Delta h_{soln} \qquad (1)$$

q is the electrical energy supplied during the experiment, Δh_v and $\Delta h_v'$ are the specific enthalpies of vaporization for the substance and for water, respectively. Δh_{soln} is the specific enthalpy of solution of water into the substance under the actual concentrations of the experiment. The molar enthalpy of vaporization of the substance, ΔH_v, is given by (2)

$$\Delta H_v = \frac{M}{a(1-0.01x)-b(1-0.01y)}[q-0.01(by-ax)(\Delta h_v'+\Delta h_{soln})] \qquad (2)$$

where *M* is the molecular weight of the substance.

RESULTS AND DISCUSSION

Table 1. Results from the determination of the enthalpy of vaporization of 2-methoxyethanol at 25.00°C.

| Amount of substance evaporated | Amount of water uptake | Electrical energy supplied | Apparent ΔH_v (no correction for water uptake) | Correction due to the water uptake by | | ΔH_v |
| | | | | condensation of water vapor | dissolution of liquid water | |
mg	mg	J	kJ/mol	kJ/mol	kJ/mol	kJ/mol
81.854	0.260	47.909	44.538	0.588	0.039	45.165
82.877	0.452	48.029	44.098	1.010	0.067	45.175
82.486	0.319	48.115	44.387	0.716	0.047	45.150
81.438	0.125	47.929	44.784	0.284	0.019	45.087
79.483	0.059	47.027	45.022	0.137	0.009	45.168
79.829	0.114	47.170	44.963	0.264	0.017	45.244
						45.17 ± 0.04

Experimental results for the individual measurements on 2-methoxyethanol are given in Table 1. Values for the weight of substance evaporated and the amount of electrical energy supplied are the corrected values.[4]

To calculate ΔH_v (eqn. 2) it is necessary to know Δh_{soln}. If this value is not known it can usually easily be determined by solution calorimetry. In the present case, however, the experiments were arranged in such a way that different quantities of water were taken up by the substance during the experiments.

The experimental results were inserted into eqn. 2 and best values were evaluated for both ΔH_v and Δh_{soln} by a least-squares fit. In the calculations $\Delta h_v'$ was taken to be 2.433 kJ/g.[4] ΔH_v was determined to be 45.17 ± 0.04 kJ/mol and Δh_{soln} to 0.16 kJ/g. By use of the derived best value for Δh_{soln}
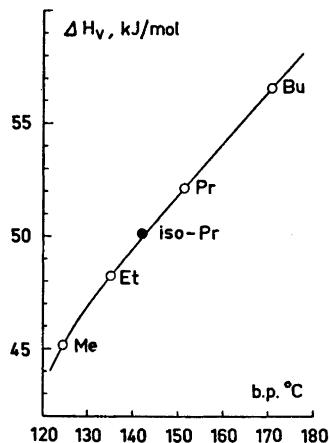

Fig. 1. Enthalpy of vaporization *versus* normal boiling point for some alkoxyethanols, $ROCH_2CH_2OH$. The boiling point for R = i-Pr was obtained from the value reported in Ref. 18 after correction to 760 mmHg. The boiling points for the other compounds were determined during this work.

the individual corrected ΔH_v values were calculated. These values, given in the last column of Table 1, show a normal spread. If, as in the present measurements, the water uptake is different in the individual runs and not too high, the corrected ΔH_v-value may be derived by a linear extrapolation of the apparent ΔH_v-values to zero water uptake.

For 2-ethoxyethanol the water uptake was smaller but the same method was used in the calculation. For all other compounds the water uptake was very small and apparent and corrected ΔH_v values were identical. In Table 2

Table 2. Enthalpies of vaporization of 2-alkoxyethanols. Values refer to the process ROCH$_2$CH$_2$OH(liq. 25°C)←ROCH$_2$CH$_2$OH(real gas, 25°C).

Substance	Number of determinations	Enthalpy of vaporization kJ/mol		
		This work	Literature values [a]	
2-Methoxyethanol	6	45.17 ± 0.04	38.2;[b] 39.3;[c] 40.2;[b] 41.4;[d] 43.1;[e] 44.73;[f] 44.83;[g] 46.0 [h]	
2-Ethoxyethanol	8	48.21 ± 0.05	39.4;[b] 41.2;[b] 45.7;[i] 46.6;[b] 47.0;[j] 47.11[f]	
2-Propoxyethanol	7	52.12 ± 0.10		
2-i-Propoxy- ethanol	6	50.12 ± 0.09		
2-Butoxyethanol	7	56.59 ± 0.02		

[a] All literature values were derived from vapor pressure relationships and refer only approximately to 25°C.

[b] From the compilation by Bondi and Simkin.[3]

[c] Gardner.[5] [d] Gallaugher and Hibbert.[6] [e] Gardner and Brewer.[7] [f] Pick *et al.*[8] [g] Boder *et al.*[9] [h] Simonetta and Barakau.[10] [i] Doolittle.[11] [j] Davis.[12]

the obtained ΔH_v values for all compounds investigated are summarized. Uncertainties given are random errors expressed as twice the standard deviation of the mean, $\pm 2\sqrt{\sum \delta^2 / n(n-1)}$. Possible systematic errors are difficult to estimate but a comparison with results from test experiments leads us to believe that the overall uncertainty for all compounds is ≤ 0.1 kJ/mol.

In Table 2 are also compiled ΔH_v values earlier reported for the two first compounds in the series. As indicated earlier these values show a very large spread and are not considered reliable. No previous investigations seem to have been reported for the other compounds.

Group enthalpy values. The CH$_2$-increment between MeOCH$_2$CH$_2$OH and EtOCH$_2$CH$_2$OH is very low, 3.0 kJ/mol. The increment for the next higher pair is larger, 3.9 kJ/mol, and it is about normal between the Pr- and the Bu-homologue, 4.5 kJ/mol. We may in this connection note that the difference in normal boiling point between the lower members in the series is exceptionally small; in particular between the two lowest members (*cf.* Fig. 1).

The difference in ΔH_v between the Pr and the i-Pr compound has a normal value, 2.0 kJ/mol.

If the present four straight chain compounds, ROCH$_2$CH$_2$O−H, are compared with corresponding ethoxy compounds,[2] ROCH$_2$CH$_2$O−Et, it is

found that the former ΔH_v values are 5.3 ± 0.3 kJ/mol higher. A similar comparison can be made between EtO $-$ H [13] and EtO $-$ Et [14] where, however, a much larger difference is found, 15.0 kJ/mol. This is interpreted as being the result of an extensive intramolecular hydrogen bonding in the gas phase for the alkoxyethanols.

Correlation between ΔH_v *and normal boiling points.* Several methods have been proposed for the estimation of enthalpies of vaporization, both at the normal boiling point and at any given temperature; see *e.g.* Refs. 15, 16. The oldest as well as the simplest is Trouton's rule which states that the entropy of vaporization at the normal boiling point is constant, (≈ 88 kJ/mol).

$$\Delta S_{bp} = (\Delta H_v/T)_{bp} = \text{const.} \tag{3}$$

Klages [17] made use of the observation that the temperature derivative of ΔH_v is roughly the same for all non-associated compounds and modified eqn. (3) to give ΔH_v at 25°C.

$$\Delta H_v = A + B \times t_{bp} \tag{4}$$

where A and B are constants (22.6 and 0.015 kJ/mol, respectively) and t_{bp} is the normal boiling point. Klages also found eqn. (4) to hold for alcohols if the constants were changed ($A = 28.5$; $B = 0.019$ kJ/mol, respectively). During the course of this series of investigations it has been verified that eqn. (4) holds rather accurately although the constants are significantly different for different groups of "non-associated" compounds. For several groups of compounds the linear relationship (4) has been found to hold precisely (boiling points have been > 200°C) whereas for some groups the $\Delta H_v/t_{bp}$ plot has given smooth weakly convex curves. A $\Delta H_v/t_{bp}$ plot for the present compounds is shown in Fig. 1. The curve is smooth but in contrast to the case for other groups investigated it is weakly concave. This is in line with the fact that t_{bp} differences increase between the successive members of the homologous series whereas the opposite is normal.

For similar molecular weights the boiling points are approximately the same for glycol ethers and alcohols indicating a similar liquid structure. However, the values for the glycol derivatives fall on a much lower $\Delta H_v/t_{tb}$ curve than those for alcohols. This agrees with the suggested gas phase intramolecular hydrogen bond stabilization for the glycol ethers.

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